IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

In re Application of: Sosa, et al.	§	
	§	
Serial No.: 10/723,656	§	Group Art Unit: 1711
	§	
Confirmation No.: 8871	§	
	§	
	§	
Filed: November 26, 2003	§	Examiner: Asinovsky
	§	
For: Use of Tetrafunctional Initiators to	§	Customer No. 25264
Improve the Rubber Phase Volume	§	
of HIPS	§	Docket No.: COS-919
	§	

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<tr><td colspan="2">CERTIFICATE OF MAILING
37 CFR 1.10
I hereby certify that this correspondence is being deposited with the United States Postal Service as First Express Class Mail in an envelope addressed to: Mail Stop Appeal Brief-Patents, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.</td></tr>
<tr><td>11/08/2005
Date</td><td>Signature</td></tr>
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Dear Honorable Commissioner:

TRANSMITTAL LETTER AND FEE AUTHORIZATION

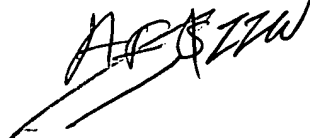In connection with the above identified application, Applicants respectfully submit the following documents:

1. Appeal Brief. *and*
2. *Article*

The Commissioner is authorized to charge the fee of $500.00, along with any additional fees that may be required for this submission, or credit any overpayments, to Deposit Account No. 03-3345.

Respectfully submitted,

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Dear Honorable Commissioner:

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APPEAL BRIEF

Applicants submit this Appeal Brief to the Board of Patent Appeals and Interferences on appeal from the decision of the Examiner of Group Art Unit 1711 dated April 18, 2005, finally rejecting claims 1-36.

Real Party in Interest

The present application has been assigned to Fina Technology Inc., P.O. Box 674412, Houston, Texas 77267.

Related Appeals and Interferences

Appellants assert that no other appeals, interferences or judicial proceedings are known to the Appellants, the Appellants' legal representative or Assignee that will

directly affect, be directly affected by or have a bearing on the Board's decision in the pending appeal.

Status of Claims

Claims 1-36 are pending in the application and were originally presented in the application. Claims 1-36 stand rejected under 35 U.S.C. §103(a). The rejection of the pending claims is appealed. The pending claims are shown in the attached Appendix A.

Status of Amendments

The Examiner indicated the allowability of dependent claims 3, 15 and 30 in the Final Office Action. Therefore, new claims 37-39 (*e.g.*, incorporation of features of dependent claims into the independent claims) were submitted in Response to the Final Office Action. However, the Examiner refused entry of the amendments. *See*, Advisory Action.

Summary of the Invention

A balance of several characteristics, including average molecular weight, molecular weight distribution, melt flow index and storage modulus, is generally required to produce polystyrene suitable for a particular application. Further, the suitability of High Impact Polystyrene (HIPS) depends on the rubber morphology, which is influenced by rubber particles size, rubber particle size distribution, swell index, grafting and the rubber phase volume (measured by the gel to rubber ratio), for example. *See*, specification, at least paragraph 2.

The gel to rubber ratio generally represents the rubber efficiency of a process, *i.e.*, how much rubber must be used to obtain similar product quality. Commercial HIPS materials generally result in a (G/R) that decreases as the swell index increases. *See*, specification, at least paragraph 20.

Unexpectedly, it has been discovered that utilizing trifunctional and tetrafunctional initiators in the HIPS process results in a trend that is contrary to conventional HIPS resins, *i.e.*, an increasing G/R with an increasing swell index. *See*, specification, at least paragraph 21. Such a trend result in higher production rates with

the ability to maintain molecular weights and improved rubber phase volumes, for example. *See*, specification, at least paragraph 25.

Issue Presented

1.   Whether the Examiner erred in rejecting claims 1-36 under 35 U.S.C. §103(a) as being unpatentable over U.S. Patent No. 6,433,092, U.S. Patent No. 6,166,099, U.S. Patent No. 6,274,641, U.S. Patent No. 6,420,444 or U.S. Patent No. 6,608,141 (collectively referred to as *Krupinski*) on grounds that *Krupinski* does not teach, show or suggest the claimed properties.

Arguments

I.   THE EXAMINER ERRED IN REJECTING CLAIMS 1-36 UNDER 35 U.S.C. §103(a) AS BEING UNPATENTABLE OVER *KRUPINSKI* BECAUSE *KRUPINSKI* DOES NOT TEACH, SHOW OR SUGGEST A COPOLYMERIZED PRODUCT HAVING A G/R THAT INCREASES AS SWELL INDEX INCREASES.

Applicants personally interviewed the pending claims with the Examiner on January 12th, 2005, where the Examiner concurred with the Applicants' argument that the process and resin of *Krupinski* are not identical to the process and resins claimed. However, the Examiner issued a Final Rejection on April 18, 2005.

In finally rejecting the claims, the Examiner submits the ratio of % gel to % rubber can be within the range specified in the present claims. *See*, Advisory Action. Applicants disagree that *Krupinski* teaches, shows or suggests a % gel to % rubber (G/R) that increases as the swell index increases.

The prior art reference must teach or suggest all of the limitations of the claims. *See*, *In re Wilson*, 424 F.2d 1382, 1385, 165 U.S.P.Q. 494, 496 (C.C.P.A. 1970.) As previously stated, *Krupinski* does not teach or suggest a ratio of % gel to % rubber (G/R) that increases as swell index increases, as recited in the pending claims.

The Examiner further states that there are no process conditions for producing the improved HIPS and that all references to *Krupinski* disclose a process for making HIPS using a tetrafunctional peroxide. *See*, Advisory Action. The process conditions are clearly recited in the pending claims (*e.g.*, copolymerizing at least one vinylaromatic
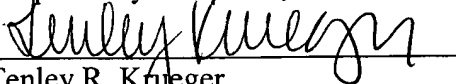
monomer with at least one diene polymer in the presence of at least one multifunctional initiator selected from the group consisting of trifunctional and tetrafunctional peroxides.)

Further, that which is inherent in the prior art, if not known at the time of the invention, cannot form a proper basis for rejecting the claimed invention as obvious under Section 103. *See, In re Shetty*, 566 F.2d 81, 86, 195 U.S.P.Q. 753, 756-57 (C.C.P.A. 1977.) The test of obviousness is statutory, rather than dictated by case law. *See, In re Ochiai*, 71 F.3d at 1569, 37 U.S.P.Q.2d at 1131. It would not have been obvious to those of ordinary skill in the art to choose trifunctional and tetrafunctional peroxides to produce a copolymerized product having a G/R that increases as swell index increases. Such an effect (*e.g.*, G/R increasing as swell index increases) was not known and in fact the contrary was believed. *See, Impact Polystyrene: Factors Controlling the Rubber Efficiency*, E.R. Wagner and L.M. Robeson, Rubber Chem. Tech., Vol. 43, pp 1129-1137, at 1131-1132 and 1135-1136 and U.S. Patent No. 6,703,460 (*Blackmon*) at Table III. Accordingly, Applicants respectfully request reversal of the rejection.

Conclusion

In conclusion, *Krupinski* nowhere teaches or suggests recovering a copolymerized product that has a ratio of % gel to % rubber (G/R) that increases as swell index increases, such as recited in the pending claims. Thus, Applicants respectfully request reversal of the rejections of claims 1-36.

Respectfully submitted,

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Appendix A

Pending Claims

1.   A method for producing an improved copolymerized product comprising:

copolymerizing at least one vinylaromatic monomer with at least one diene polymer in the presence of at least one multifunctional initiator selected from the group consisting of trifunctional and tetrafunctional peroxides, and

recovering a copolymerized product that has a ratio of % gel to % rubber (G/R) that increases as swell index increases.

2.   The method of claim 1 where the copolymerized product has a melt flow index (MFI) ranging from about 2 to about 7.

3.   The method of claim 1 where the G/R increases from about 1 to about 4 as the swell index increases from about 8 to about 20.

4.   The method of claim 1 where in copolymerizing the monomer, the vinylaromatic monomer is styrene.

5.   The method of claim 1 where in copolymerizing the monomer, the multifunctional initiator is selected from the group consisting of tri- or tetrakis t-alkylperoxycarbonates, tri- or tetrakis (polyether peroxycarbonate), tri- or tetrakis-(t-butylperoxycarbonyloxy) methane, tri- or tetrakis-(t-butylperoxycarbonyloxy) butane, tri- or tetrakis (t-amylperoxycarbonyloxy) butane and tri- or tetrakis (t-C_{4-6} alkyl monoperoxycarbonates), and mixtures thereof.

6.   The method of claim 1 where the copolymerized product is more highly branched as compared with a polymerized product made by an otherwise identical method except that a multifunctional initiator replaces at least a portion of a difunctional initiator.

7.   The method of claim 1 where the multifunctional initiator is present in an amount ranging from about 50 to about 1200 ppm, based on the vinylaromatic monomer.

8.   The method of claim 1 where in copolymerizing the monomer, the polymerizing is conducted at a temperature between about 110°C and about 180°C.

9.   The method of claim 1 where the weight ratio of vinylaromatic monomer to diene polymer ranges from about 97:3 to about 85:15.

10.   The method of claim 1 where in recovering the product, the copolymerized product is high impact polystyrene (HIPS).

11   The method of claim 1 where the polymerization rate ranges from about 2 to 7 times that of styrene polymerized thermally in the absence of initiator.

12   The method of claim 1 where the polydispersity of the copolymerized product ranges from about 2.3 to about 4.0.

13.   An improved copolymerized product made by the process comprising:

       copolymerizing at least one vinylaromatic monomer with at least one diene polymer in the presence of at least one multifunctional initiator selected from the group consisting of trifunctional and tetrafunctional peroxides, and

       recovering a copolymerized product that has a ratio of % gel to % rubber (G/R) that increases as swell index increases.

14.   The copolymerized product of claim 13 where the copolymerized product has a melt flow index (MFI) ranging from about 2 to about 7.

15.   The copolymerized product of claim 13 where the G/R increases from about 1 to about 4 as the swell index increases from about 8 to about 20.

16.   The copolymerized product of claim 13 where in copolymerizing the monomer, the vinylaromatic monomer is styrene.

17.   The copolymerized product of claim 13 where in copolymerizing the monomer, the multifunctional initiator is selected from the group consisting of tri- or tetrakis t-alkylperoxycarbonates, tri- or tetrakis (polyether peroxycarbonate), tri- or tetrakis-(t-butylperoxycarbonyloxy) methane, tri- or tetrakis-(t-butylperoxycarbonyloxy) butane, tri- or tetrakis (t-amylperoxycarbonyloxy) butane and tri- or tetrakis (t-C_{4-6} alkyl monoperoxycarbonates), and mixtures thereof.

18.   The copolymerized product of claim 13 where in recovering the copolymerized product, the product is more highly branched as compared with a polymerized product made by an otherwise identical method except that a multifunctional initiator replaces at least a portion of a difunctional initiator.

19.   The copolymerized product of claim 13 where in the copolymerizing the multifunctional initiator is present in an amount ranging from about 50 to about 1200 ppm, based on the vinylaromatic monomer.

20.   The copolymerized product of claim 13 where in the copolymerizing the polymerization rate ranges from about 2 to 7 times that of styrene polymerized thermally in the absence of initiator.

21   The copolymerized product of claim 13 where the polydispersity of the copolymerized product ranges from about 2.3 to about 4.0.

22.   The copolymerized product of claim 13 where in copolymerizing the monomer, the polymerizing is conducted at a temperature between about 110°C and about 180°C.

23.   The copolymerized product of claim 13 where in copolymerizing the monomer, the weight ratio of vinylaromatic monomer to diene polymer ranges from about 97:3 to about 85:15.

24.   The copolymerized product of claim 13 where in recovering the product, the polymerized product is high impact polystyrene (HIPS).

25.   An article made with the vinylaromatic/diene graft copolymer of claim 13.

26.   A resin comprising:

at least one vinylaromatic monomer;

at least one diene polymer;

at least one multifunctional initiator selected from the group consisting of trifunctional and tetrafunctional peroxides, where the amount of multifunctional initiator is sufficient to produce a copolymerized product that has a % gel to % rubber (G/R) ratio that increases as swell index increases.

27.   The resin of claim 26 where the amount of multifunctional initiator is sufficient to polymerize the vinylaromatic monomer at a rate of from about 2 to 7 times that of styrene polymerized thermally in the absence of initiator.

28.   The resin of claim 26 where the amount of multifunctional initiator is sufficient to produce a copolymerized product having a polydispersity ranging from about 2.3 to about 4.0.

29.   The resin of claim 26 where the amount of multifunctional initiator is sufficient to produce a copolymerized product that has a melt flow index (MFI) ranging from about 2 to about 7.

30.   The resin of claim 26 where the G/R increases from about 1 to about 4 as the swell index of the product made therefrom increases from about 8 to about 20.

31.   (Original)   The resin of claim 26 where the vinylaromatic monomer is styrene.

32.   The resin of claim 26 where the multifunctional initiator is selected from the group consisting of tri- or tetrakis t-alkylperoxycarbonates, tri- or tetrakis (polyether peroxycarbonate), tri- or tetrakis-(t-butylperoxycarbonyloxy) methane, tri- or tetrakis-(t-butylperoxycarbonyloxy) butane, tri- or tetrakis (t-amylperoxycarbonyloxy) butane and tri- or tetrakis (t-C_{4-6} alkyl monoperoxycarbonates), and mixtures thereof.

33.   The resin of claim 26 where the copolymerized product made therefrom is more highly branched as compared with a polymerized product made by an otherwise identical method except that a multifunctional initiator replaces at least a portion of a difunctional initiator.

34.   The resin of claim 26 where in the multifunctional initiator is present in an amount ranging from about 50 to about 1200 ppm, based on the vinylaromatic monomer.

35.   The resin of claim 26 where the weight ratio of vinylaromatic monomer to diene polymer ranges from about 97:3 to about 85:15.

36.   An article made from the resin of claim 26.

Appendix B

Evidence

1. *In re Wilson*, 424 F.2d 1382, 165 U.S.P.Q. 494 (C.C.P.A. 1970.)

2. *In re Shetty*, 566 F.2d 81, 195 U.S.P.Q. 753 (C.C.P.A. 1977.)

3. *In re Ochiai*, 71 F.3d 569, 37 U.S.P.Q.2d 1131.

4. *Impact Polystyrene: Factors Controlling the Rubber Efficiency*, E.R. Wagner and L.M. Robeson, Rubber Chem. Tech., Vol. 43, pp 1129-1137.

5. U.S. Patent No. 6,703,460.

IMPACT POLYSTYRENE: FACTORS CONTROLLING THE RUBBER EFFICIENCY

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INTRODUCTION

Impact polystyrene is a composite consisting of a continuous rigid poly-styrene phase and a dispersed rubber phase containing occlusions of poly-styrene. Basic papers on impact polystyrene deal with the mechanical loss characteristics of butadiene based rubbers[1] used as impact modifiers, the formation[2-4] and morphology[5] of the dispersed rubber phase, processing details[6,7], and the mechanism of energy absorption[8,9] during impact. Few papers, however, deal with the concept of rubber efficiency in impact polystyrene[10].

Though impact strength is only one of several desired properties such as processibility and surface appearance, it is the most important end-use property of impact polystyrene. A very challenging objective of fundamental research on impact polystyrene is the achievement of maximum impact strength at the lowest possible rubber content in the composite. This task can not be solved without a deeper insight into those parameters which control the impact strength of the composite. Next to the type and amount of rubber, the amount of the rubber phase volume (rubber + occluded polystyrene), the degree of crosslinking of the rubber, and the molecular weight distribution of the matrix polystyrene have emerged as the prime parameters affecting impact strength. This paper deals with the quantitative assessment and interrelation that these parameters have on rubber efficiency. Rubber efficiency is defined as the ratio: Impact Strength/per cent rubber in impact polystyrene.

RESULTS AND DISCUSSION

RUBBER PHASE VOLUME: DEPENDENCE ON AGITATION

Rubber phase volume studies were carried out on composites prepared by the batch polymerization of styrene in the presence of polybutadiene rubber of microstructure: 35% cis-1,4; 55% trans-1,4; 10% 1, 2 addition. It is a charac-teristic of this technique that the rubber which is solvated by styrene tends to go through a phase inversion after sufficient polystyrene has been formed[4]. Provided the rate of agitation during the subsequent polmerization of styrene is maintained constant, the final rubber-microgels are very close in size to that distribution which was adjusted at the phase inversion[11].

All other conditions being equal, the final rubber phase volume depends on the size of the rubber microgels. In order to define the limits of this obser-vation, styrene solutions containing 7% polybutadiene rubber were polymerized at three different rates of agitation at a constant heat-time cycle. As seen in Table I, the rubber phase volume increases rapidly with decreasing agitation. It must be noted that particle size, rubber phase volume, and agitation are

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TABLE I

EFFECT OF AGITATION ON RUBBER PHASE VOLUME

RPM	200	35	
Average gel size, μ	2	10	>1000
Rubber vol, %	7	7	7
Rubber phase vol, %	18	37	80
Rigid phase vol, % PS	82	63	20

interrelated. The rubber phase volume was determined from the weight per cent insolubles obtained after separation of the matrix polystyrene in 50:50 methyl ethyl ketone-acetone. A similar procedure is described in reference 10.

MECHANISM OF INCREASING RUBBER PHASE VOLUME

Two impact polystyrenes containing 6% polybutadiene but 22%, and 78% rubber phase volume were prepared. The morphology of the microgels is illustrated in electron photomicrographs (Figures 1 and 2). These figures show
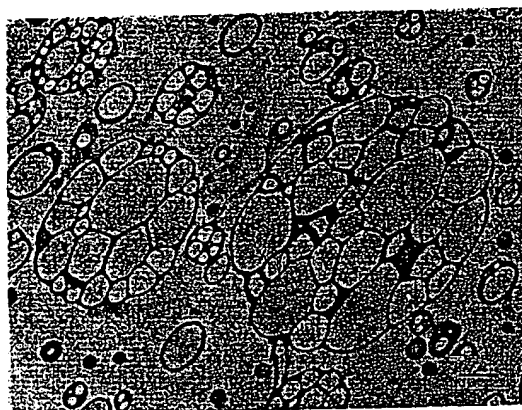
Fig. 1.—Rubber membrane structure of impact polystyrene (6% polybutadiene; 22% rubber phase volume).
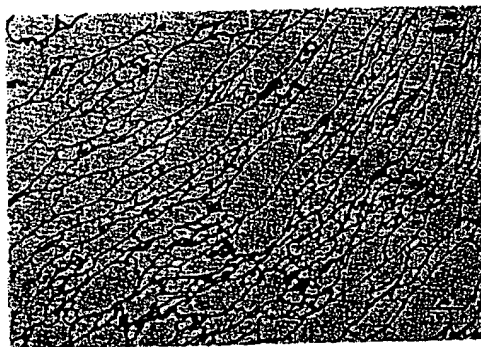
Fig. 2.—Rubber membrane structure of impact polystyrene (6% polybutadiene; 78% rubber phase volume).

that the rubber phase volume is increased from 22 to 78% by occlusion of
polystyrene within the rubber membrane structure as has been previously
observed[12,13].

Phase microscopic investigations revealed that rupture of the rubber membranes during agitation is the major factor causing small rubber gel particles
and lower rubber phase volume. The agitation has, therefore, shifted the equilibrium towards the complete separation of the polybutadiene-styrene and
polystyrene-styrene phases and towards the ultimate formation of homogeneous
rubber gels consisting of crosslinked polybutadiene grafted with polystyrene.
With decreasing rate of agitation, the final rubber phase particles are more
heterogeneous due to the increasing volume of occluded polystyrene trapped
within rubber membranes which has not been removed by shearing forces.

The rubber phase volume and gel size distribution affect several properties
which include impact strength, surface appearance, processibility, and stress-strain characteristics. In this paper, the effect of rubber phase volume on impact
strength and tensile modulus are considered.

EFFECT OF GEL PHASE VOLUME ON THE MECHANICAL CHARACTERISTICS OF IMPACT POLYSTYRENE

Using a free vibration torsion pendulum based on the design of Nielsen[14],
mechanical loss spectra were obtained over a range of 0.5 to 2 cps on 20 mil
thick compression molded specimens. Mechanical loss curves of two impact
polystyrenes of equal rubber phase volume (22%) but different rubber content
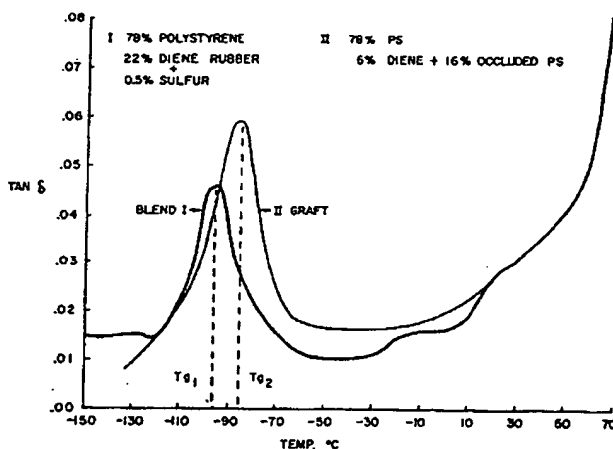(6% and 22%) are illustrated in Figure 3. It is apparent that occluded poly-

Fig. 3.—Mechanical loss curves of impact polystyrene containing similar
rubber phase volume with different rubber content.

styrene is able to substitute for rubber. The effect of increasing the rubber
phase volume at constant rubber content on the position of the glass transition
of rubber phase and the magnitude of the mechanical loss curve is shown in
Figures 4 and 5. By increasing the rubber phase volume by occlusion of poly-
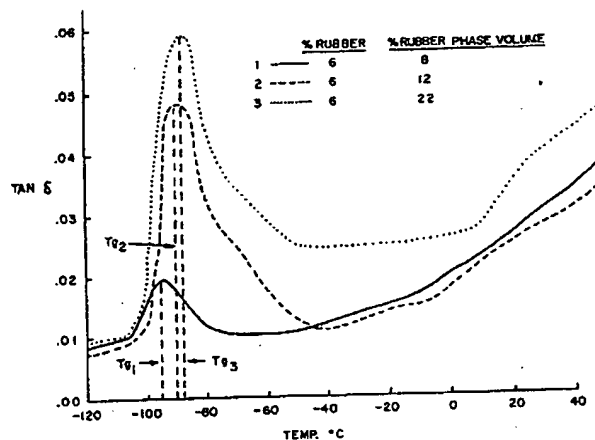
Fig. 4.—Mechanical loss curves for similar rubber content (6%) with varying rubber phase volume in impact polystyrene.

styrene, the magnitude of the mechanical loss curve is dramatically increased due to the substitution of occluded polystyrene. The T_g of the rubber is increased due partially to the increase in grafted polystyrene with increasing gel volume. The analysis of the gel phase of these samples for graft polymer after removal of occluded polystyrene showed that the graft polymer content increased with the rubber phase volume from 10 to 90% based on rubber concentration while the experimental crosslink density remained constant. The increase in graft polymer content with rubber phase volume is tentatively explained by the availability of the very thin expanded rubber membranes
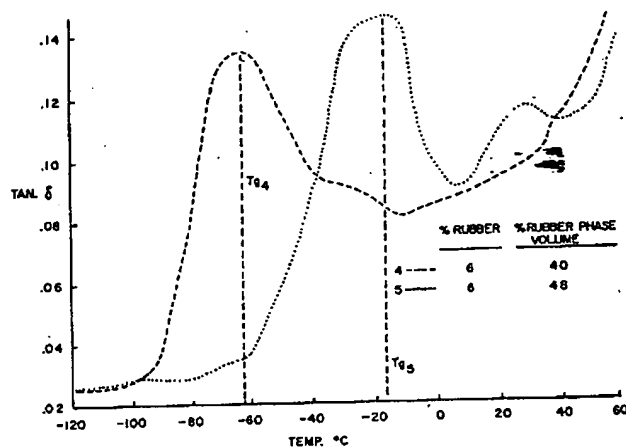
Fig. 5.—Mechanical loss curves for similar rubber content (6%) with varying rubber phase volume in impact polystyrene.

for grafting. Other factors which may affect the glass transition position will be surface area between rubber/polystyrene and the true crosslink density. It must be noted that the breadth of the transition increases indicating increasing heterogeneity of the rubber caused by nonuniform grafting and crosslinking.

The mechanical properties were obtained on 10 mil compression molded specimens cut into $\frac{1}{8}$ in. strips. The data shown in Table II for constant rubber concentration shows a marked decrease in tensile modulus with increasing rubber phase volume as one would expect from the rubber phase mechanical loss transition which also increase in magnitude. The impact strength is determined from the calculations of the work required to break a specimen held normal to the line of force of a pendulum. It is of interest to note that both the elongation at break and impact strength pass through maxima as the rubber phase volume is increased.

TABLE II
EFFECTS OF RUBBER PHASE VOLUME[a]

Phase volume %	T_{gR} °C	Tensile modulus, psi $\times 10^{-3}$	Pendulum impact[b], ft lbs/in.[3]	Elongation at break, %
6	−110	400	5	3
12	−95	350	23	20
22	−87	280	140	45
30	−55	150	68	34
78	—	80	15	8

[a] $R = 6\%$.
[b] 10 mil film.

Two theories which yield similar results and adequately relate the tensile modulus as a function of rubber phase volume are Kerner's[15] and Hashin's[16]. For the case of the rubber phase modulus $\ll$ polystyrene matrix modulus, Kerner's equation reduces to:

$$E = \frac{E_c \phi_c (7 - 5\nu_c)}{15\phi_d(1 - \nu_c) + \phi_c(7 - 5\nu_c)}$$

and Hashin's obtains:

$$E = E_c\left[1 - 15\left(\frac{1 - \nu_c}{7 - 5\nu_c}\right)\phi_d\right],$$

where E = modulus of the composite, E_c = modulus of the continuous phase, E_d = modulus of the dispersed phase, ν_c = Poisson's ratio, $\nu_c = 0.35$ for polystyrene, ϕ_c = volume fraction continuous phase, ϕ_d = volume fraction dispersed phase.

Experimental data at constant rubber concentration (6%) shows that both theories approximate the modulus data (Figure 6) at low volume fraction rubber phase volume. This observation points out that occluded polystyrene can substitute for rubber if $E_d \ll E_c$. As the magnitude of the mechanical loss peak for the rubber transition is related to the drop in modulus through the rubber glass transition, the observed substitution of occluded polystyrene for rubber is interrelated in terms of modulus and mechanical loss peak magnitude.

It has been shown by Holliday[17] that the relative modulus of ABS as a function polybutadiene volume fraction can be approximated by Kerner's and Hashin's equations. However, this data indicate that the *rubber phase volume*, ϕ_d, and not the rubber content is the determining factor for tensile modulus and mechanical loss peak magnitude.

The maxima in impact strength and ultimate elongation at an intermediate rubber phase volume is an important factor in optimizing rubber efficiency. Two reasons for this are the variation in the modulus of the rubber phase and the rubber phase particle size. Bucknall[9] and Keskkula and Turley[10] have indicated that the rubber phase modulus determines the stress concentration in the matrix phase and, therefore, will influence the craze formation. At
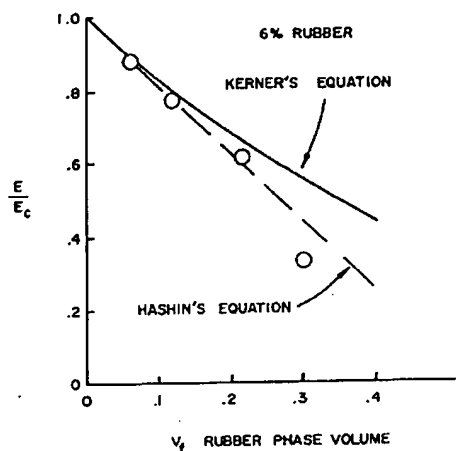
Fig. 6.—Impact polystyrene tensile modulus data compared to Kerner's and Hashin's theories.

constant rubber concentration as the rubber phase volume increases, the rubber phase modulus increases. As will be shown, increasing the rubber phase modulus by crosslinking the rubber has an adverse effect on both impact strength and ultimate elongation. It has been pointed out by Bender[11] and Willersim[18] that the particle size also plays an important role in determining the impact strength. Small particles are ineffective, as propagating cracks can engulf the rubber particles. Large particle size is not an efficient utility of the rubber phase, as the surface/volume ratio is diminished thus diminishing the magnitude of craze formation. As one can see from Table I, increasing the rubber phase volume results in dramatic increases in the particle size. While it is not the intent of this report to assess quantitatively the relation between the rubber phase modulus and particle size on impact strength, the observed data qualitatively agree with previously published observations. Thus, the observed maxima of impact strength and ultimate elongation at an intermediate rubber phase volume are due to the optimization of opposing factors. Increasing occluded polystyrene (rubber phase volume) increases the matrix-rubber phase surface area available for craze formation up to a point where further occlusions increase particle size and rubber phase modulus beyond their optimum level.

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EFFECT OF CROSSLINKING ON THE MECHANICAL CHARACTERISTICS OF IMPACT POLYSTYRENE

Before solution polymerization with styrene, polybutadiene rubber has a tensile modulus of ~200 psi. During the polymerization of styrene, polybutadiene is both grafted and crosslinked. The mechanical properties of the rubber phase of an impact polystyrene of 6% rubber and 22% rubber phase volume (determined by compression molding the rubber phase after extraction from the polystyrene matrix) were found to be: tensile modulus = 15,000 psi; tensile strength = 2000 psi.; and ultimate elongation = 150%. A precise characterization of the crosslink density of the rubber-polystyrene graft polymer can only be made after removal of occluded polystyrene from the gel. However,
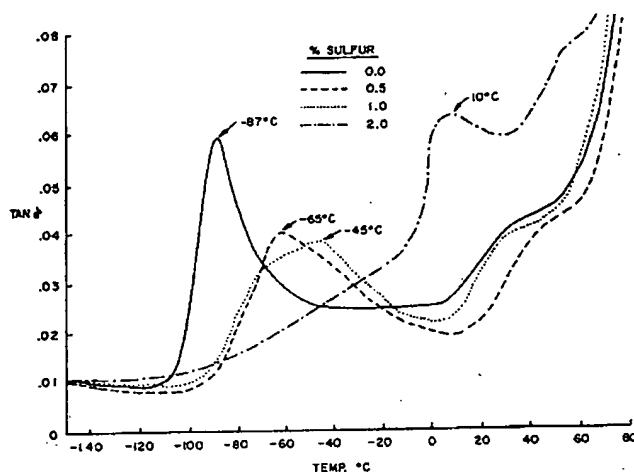

FIG. 7.—Effect of crosslinking rubber in impact polystyrene on the mechanical loss characteristics.

the swelling index of the heterogeneous rubber phase can be used to characterize the crosslink density semi-quantitatively. The swelling index of the insolubles in impact polystyrene was measured after equilibrium swelling of the microgels in toluene for 48 hours.

The effect of crosslinking of the rubber in impact polystyrene on mechanical loss and mechanical property characteristics was studied by crosslinking with sulfur. Increasing amounts of sulfur were added to impact polystyrene and mixed and compression molded at a constant temperature-time cycle. Rubber phase volume measurements taken after crosslinking showed no change from the control.

A shift in the rubber phase T_g to higher temperature with increasing amounts of sulfur addition is shown in the mechanical loss curves in Figure 7. The broadening of the damping peak is also observed and can be considered to be caused by increasing heterogenity as observed with other systems[19].

The shift in the glass transition, which is induced by crosslinking, exerts a profound effect on the modulus, impact strength, and ultimate elongation of impact polystyrene (Table III). Generally, impact strength and elongation pass

TABLE III

EFFECTS OF CROSSLINKING[a]

Sulfur %	Swelling index[b]	T_{on}, °C	Tensile-modulus, psi × 10⁻³	Elongation at break, %	Pendulum impact[c] ft-lb/in.[?]
0.0	12	−87	240	40	140
0.5	10	−65	260	32	100
1.0	9	−45	280	25	59
2.0	5	+10	360	2	2

[a] Impact polystyrene, R = 6%, RPH = 22%.
[b] Toluene.
[c] 10 mil film.

through a maximum at a swelling index (toluene) range of 10–14. From the nature of the morphology of impact polystyrene, it is obvious that if the rubber were not crosslinked at all or only slightly crosslinked, the occluded polystyrene particles would be able to coalesce with the matrix during melt processing. At high levels of crosslinking, the modulus of the rubber phase is increased to the point that the stress concentration at the matrix-rubber phase interface starts decreasing thus hindering craze formation[9].

THE EFFECT OF MOLECULAR WEIGHT OF MATRIX POLY-STYRENE ON MECHANICAL CHARACTERISTICS OF IMPACT POLYSTYRENE

The physical properties of unmodified polystyrene depend upon the weight and number average molecular weights of the polymer molecules. As mentioned by Merz and coworkers[20] the physical properties of matrix polystyrene are controlled by the amount of low molecular weight species present, commonly called the "low molecular weight tail." M_w and M_n values of matrix of commercial thermally initiated impact polystyrenes are in the range of 250,000 and 70,000 respectively.

The effect of the molecular weight distribution of the matrix on rubber efficiency was defined by blending increasing amounts of polystyrene of $M_w = 32,000$ and $M_w \sim 300,000$ into an impact polystyrene of high rubber efficiency. The blends with the same volume fraction of polystyrene had similar mechanical loss curves but different mechanical properties as shown in Table IV.

TABLE IV

EFFECT OF M_w OF POLYSTYRENE ON IMPACT STRENGTH

Base IPS	PS added, %	PS M_w	R%	Elongation at break, %	Pendulum impact, ft-lbs/in.[?]
100	0	—	6.0	57	140
95	5	32,000	5.7	51	89
90	10	32,000	5.4	33	42
67	33	32,000	4.0	1	2
95	5	305,000	5.7	52	135
90	10	305,000	5.4	43	120
67	33	240,000	4.0	39	82

ation eak, ; o	Pendulum impact ft-lb/in.²
.0	140
.2	100
.5	59
2	2

of 10–14. From the us that if the rubber ccluded polystyrene melt processing. At e is increased to the iase interface starts

ATRIX POLY-ISTICS OF

nd upon the weight cules. As mentioned rix polystyrene are present, commonly s of matrix of com-ie range of 250,000

e matrix on rubber of polystyrene of rene of high rubber ystyrene had similar s as shown in Table

ENGTH

ngation break, %	Pendulum impact, ft-lbs/in.²
57	140
51	89
33	42
1	2
52	135
43	120
39	82

The blends containing polystyrene of $M_w = 32,000$ exhibited a rapid deterioration of properties as compared to the gradual decline with addition of polystyrene of $M_w \sim 300,000$. The molecular weight distribution of the matrix is, therefore, an important variable determining the ultimate properties of impact polystyrenes.

CONCLUSIONS

The rubber phase volume (rubber + occluded polystyrene) can be widely varied in impact polystyrene by controlling the rate of agitation during polymerization. The tensile modulus and magnitude of the rubber phase mechanical loss transitions are related to the degree of polystyrene occlusion. It is shown that the occluded polystyrene can substitute for rubber in determining these parameters. Impact strength and ultimate elongation pass through maxima as the rubber phase volume is increased at constant rubber concentration due to the optimization of rubber phase volume with particle size and rubber phase modulus. Over crosslinking of the rubber and a high concentration of a low molecular weight tail of matrix polystyrene have deleterious effects on the impact strength and ultimate elongation. The optimization of these three factors is required in making efficient use of the rubber in impact polystyrene.

ACKNOWLEDGMENTS

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